

Columbia Yellow
Its Structure and Related Intermediates



DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE FACULTY OF PURE SCIENCE OF COLUMBIA
UNIVERSITY

BY

FRANK H. BERGEIM, B.S., M.S.

NEW YORK CITY

1924



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UNCLASSIFIED

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TO MY
FATHER AND MOTHER

ACKNOWLEDGMENT

The author is pleased to have this opportunity of expressing his thanks to Professor Marston Taylor Bogert for his helpful guidance thruout this investigation. Without his valuable suggestions this work could not have been completed. His congenial association in the laboratory has always been a source of inspiration.

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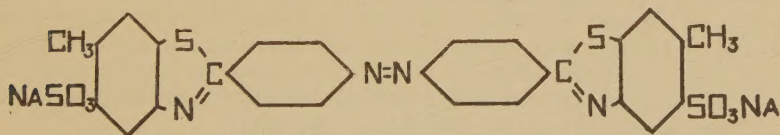
Columbia Yellow

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ABSTRACT OF DISSERTATION

The purpose of this investigation was to make a thorough study of the properties of a dye known by the name of Columbia Yellow with the hope of obtaining data that would give us a clue as to its structural constitution. It was hoped that by solving this constitution we might learn what parts of the molecule were responsible for cotton fastness, which were responsible for color, and in what general type of dye we might expect the properties of unusual stability and fastness which Columbia Yellow exhibits. Such information would have a commercial as well as theoretical interest.

Two methods of attack were used in pursuing this research. The commercial product was carefully purified and analytical results were obtained both qualitative and quantitative. The second method of attack was to build up the dye synthetically by a method differing from that used in the industry, and one which would leave little doubt regarding the constitution of the end product. Our synthetic method led to the production of a yellow dye identical in color and fastness with commercial Columbia Yellow. In brief the commercial method involves the oxidation of an amino derivative of a benzothiazole to what we now believe to be an azo compound. Our method is the reverse of this in the sense that it depends on reduction rather than oxidation. We reduced a nitro derivative of a benzothiazole analogous to the above amino compound, by the method which is most commonly used in the preparation of an azo type of compound. The azo products formed by both methods gave us fast yellow dyes which we were unable to distinguish from each other either in chemical properties or fastness on the fibre. Our results indicate that the most probable structure of Columbia Yellow is the following:



By preparing a dye which had all of the groups present in the above compound excepting the methyl groups we were able to conclude that the methyl groups were essential only to deepen the shade. This dye lacking the methyl groups was a paler yellow than Columbia Yellow but still retained the property of fastness to cotton.

We further showed that the NH_2 on the 2-phenyl part of the molecule was essential to color formation. This was done by making a compound of the same structure as the amine mentioned above in the commercial preparation of Columbia Yellow, with the one exception that the NH_2 group was replaced by an OH group. This hydroxy compound gave no color whatever with the oxidation methods used for preparing Columbia Yellow.

Several dye intermediates were prepared during the course of the work only a few of which were new. The new intermediates are the following:

- 2(p-hydroxy phenyl) 6-methyl benzothiazole-5-sulphonic acid.
- 2(p-amino phenyl) benzothiazole-6-(?) sulphonic acid.
- 2(p-nitro phenyl) 6-methyl benzothiazole.
- 2(p-azo phenyl) 6-methyl benzothiazole.

During the course of the analytical work on the commercial Columbia Yellow we developed a new method for the purification of sulphonic acid dyes. Considerable time was spent in checking up the properties already reported on Columbia Yellow and adding new data to this list of properties.

INTRODUCTORY

"It would be extremely valuable if we could know what composition a dye should have in order to dye cotton directly. Unfortunately however, in spite of the enormous amount of experimental evidence available we are still far from arriving at a satisfactory answer to this question." This statement is taken from Georgievics Textbook of Dye Chemistry (39). From this it may be seen that the very limited investigation which we undertook could only hope to add in an empirical way to the information on direct cotton dyes. The particular dye which we studied is known by the name of Columbia Yellow.

There are several reasons why we chose Columbia Yellow from a list of cotton dyes of unknown constitution. Its extreme stability toward reducing and oxidizing agents (37) made it seem questionable that the dye should have an azo structure as was intimated in the original patent (12), with very little experimental data in support of such a structure. Either the dye was a new type of azo dye with properties of stability unusual for azo types or some entirely different constitution must be assigned to it. The small amount of experimental evidence published to date leaves one conclusion as probable as the other.

Aside from the theoretical interest that a study of this kind would have there is a commercial interest which is hardly less important. Columbia Yellow has the best fastness of all cotton yellows (38). It was the most extensively used direct yellow before the war (38). An understanding of the structure of this extremely fast dye might open up cheaper methods for preparing the dye itself or suggest modifications to change the shade and yet retain the cotton fastness. We have succeeded in obtaining ex-

perimental data which has thrown some light on both of these points. These results are discussed under the heading the Constitution of Columbia Yellow.

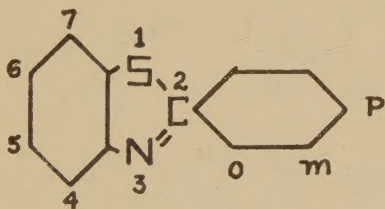
Columbia Yellow was first prepared in 1892 (12). Since that date various trade periodicals have reported results of interest to the dyer but no systematic study has been made from the viewpoint of chemical reactions and constitution. It was with this later viewpoint in mind that we made a study of Columbia Yellow.

COMMERCIAL, NAMES OF COLUMBIA YELLOW

Because of the general secrecy in industrial concerns regarding methods of preparing their dyes it is rather difficult to assign a definite formula to commercial names. It is very probable however that all of the names in the following list refer to Columbia Yellow. The Schultz number of the dye is 617 (45).

Chloramine Yellow, C GG, HW, M, FF, W extra, and RC (By); Chloramine Yellow (S); Oxyphenine Gold (ClCo); Diamine echt gelb B, C, FF, (C); Thiophosphine J (LP); Direct echt gelb BN (L); Benzamine echt gelb B (WDC); Columbia gelb (A); Vigoreux gelb (M); Chlorophosphine V (ClCo); Oxy dianil gelb G, O, (M); Napthamine gelb N (K); Direct Fast Yellow (Sch); Triazol echt gelb G, 2G, (Gr-E); Pontamine Yellow NNX (DuPont); Diphenyl Chlorine Yellow FF (G).

In naming intermediates related to Columbia Yellow we have used the following notation which is in agreement with Meyer-Jacobson and previous dissertations on benzothiazoles at Columbia University (44)



METHODS OF PREPARING COLUMBIA YELLOW

The original method for preparing Columbia Yellow as given in a German patent is as follows. "Fifty kg. of dehydrothiop-toluidine sulfonic acid were dissolved in 100 litres of water by adding 8 to 10 kg. of soda. This solution was treated at 10-15 degrees with a solution of NaOCl prepared by treating 50 kg. of bleaching powder with the calculated amount of soda. On first mixing the solution is colorless having a weak violet fluorescence. The solution soon becomes cloudy and then takes on a deep reddish color. The reaction is complete at the end of 24 hours. The

dye is then precipitated by salting out with NaCl, filtered and washed with NaCl solution until no more hypochlorite is found in the washings."

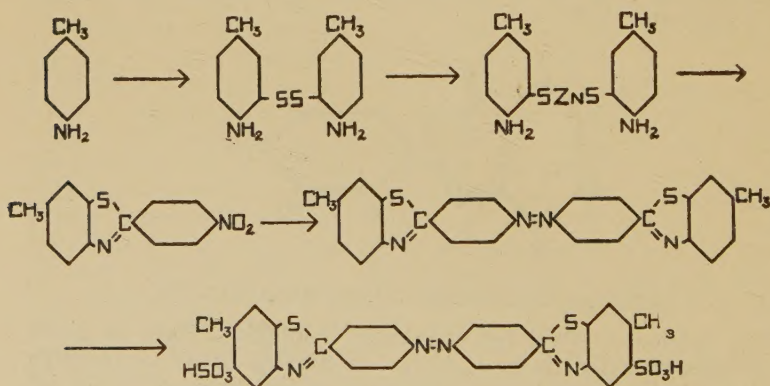
Two other methods are also mentioned in this patent. One makes use of alkaline potassium ferricyanide, and the other uses lead peroxide as the oxidizing agent. Details are given in the patent.

Another method which has been reported (17) is that of oxidizing the diazonium salt of dehydrothio-p-toluidine with NaOCl. This method is essentially the same as that of the original German patent. The claim is made that this method gives a purer and redder shade.

Green (33) gives a method starting with the ammonium salt of dehydrothio-p-toluidine sulphonic acid. In the commercial preparation of dehydrothio-p-toluidine it is obtained in a pure state as the ammonium salt of the mono sulfonate. Green's method is undoubtedly the one most commonly used in the industrial preparation of Columbia Yellow.

The best laboratory directions for preparing pure Columbia Yellow are given by Fierz (40). He uses hypochlorite oxidation of the sodium salt of dehydrothio-p-toluidine sulfonic acid.

All of the above methods depend upon the oxidation of an amino compound to an azo compound. The new method which we have developed is the reverse of these methods in that it depends on reduction rather than oxidation. The series of reactions involved in our method are given below. (See experimental part for details of carrying out).



PROPERTIES OF COLUMBIA YELLOW REPORTED IN THE LITERATURE

No article has appeared in the literature giving quantitative analytical data on the dye Columbia Yellow. The information published to date relates largely to its value as a direct cotton dye and will be found in patents and trade periodicals. For the benefit of later workers in this field we have taken the liberty of recording rather completely in a systematic way this scattered information.

Physical Properties

The dye is a brown powder (12) (grayish yellow-ref. 14) easily soluble in water. It is insoluble in conc. NaOH. Dissolves in conc. sulfuric or nitric acid to form a reddish brown solution. (blood red-ref. 14). It is reprecipitated from these acid solutions as a brownish yellow precipitate on diluting with water. Soluble in conc. HCl (we have found the solubility to be very small) forming a brown solution and is reprecipitated again by diluting with water. It is insoluble in alcohol and its spectrum in water (45) gives partial absorption in the blue and violet.

Chemical Properties

Alkali causes no change in a water solution of the dye. (14) Zinc dust decolorizes it with difficulty and air oxidation regenerates the dye again (14). It is decomposed by warming with stannous chloride and HCl (our observations do not agree with this. See exp. part). It cannot be diazotized indicating the absence of an amino group (12). It is very resistant to oxidizing and reducing agents (no specific examples are given) (37).

Behavior on the Fibre

It is very stable toward light, acids and chlorine (14). It is identified by its absolute fastness to alkali and chlorine (12). Hayes (38) gives the most complete discussion of any of the references on Columbia Yellow. According to this article Columbia Yellow was the most extensively used direct yellow before the war. The present high price has cut down its use to some extent. It has the best fastness taking everything into consideration of all the cotton yellows. It is noted for its level dyeing properties. Dyed as a union color it comes into extensive use as it dyes both cotton and wool the same shade. Owing to its level dyeing properties it makes an excellent color for shading and redyeing. Dyeings made on silk are absolutely fast to washing and water. It is hardly altered by organic or mineral acids. It is fast to stoving and hot pressing. It stands 1 degree Tw. solution of chlorine excellently. Hydrosulfite of soda does not discharge the color.

It is used for effect work. For this type of work the material is dyed with a dischargeable color and the discharge paste is mixed with Columbia Yellow and printed on and steamed under pressure. By this means the original color is discharged and the yellow is printed on in its place giving the two colors. After treated with metallic salts it becomes slightly faster. Diazotized the shade stands up well and it is really the best yellow to use for shading diazotized dyeing. Used as sulfur color the shade becomes redder and is faster to light than any of the sulfur yellows. A considerable amount of the dye is used to dye cotton knit goods the so-called Egyptian shade. Its extreme fastness to alkali makes it possible to mercerize cotton dyed with this color without injuring the shade (30).

The fastness tests have been graded by Schultz (45) in the following way. 1 indicates the highest degree of fastness and 5 the lowest. For Columbia Yellow: Rubbing-1, Hot pressing 2-1, Alkali 2-1, HCl-2, Acetic-1, Chlorine-1, Water fastness-4, Washing 3-4, Felting fastness (1) change of shade 1-2, (2) bleeding on white-3, boiling with soda (1), change of shade-3-4. (2) bleeding-4, boiling with acids (4% sulfuric), change in shade-3, bleeding-4, perspiration test (1) change of shade-1, (2) bleeding-2-3. *Methods of Dyeing with Columbia Yellow*

The catalogue of the Berlin Aniline Works (30) gives the following procedure.

For light shades:

3-5% soap (if desired 1% soda ash)
5-10% Glaubersalt cryst.

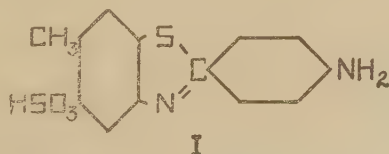
For medium shades:

2% soda ash (or 3-5% soap)
10-30% Glaubersalt cryst.

Knecht in his Manual of Dyeing (24) gives directions for dyeing cotton wool, silk, unions, and satin with Columbia Yellow. Whittaker (42) gives excellent directions for carrying out direct dyeing tests in general. In the experimental part of this dissertation will be found the method which we used in our work.

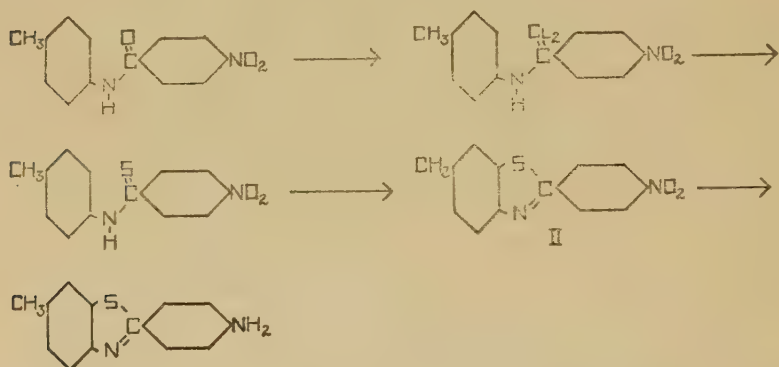
THE CONSTITUTION OF COLUMBIA YELLOW

The dye intermediate dehydrothio-p-toluidine is the intermediate used in the preparation of all commercial brands of Columbia Yellow. The constitution has been proven by several investigators to be the following (8, 9, 10, 11, 12, 48).

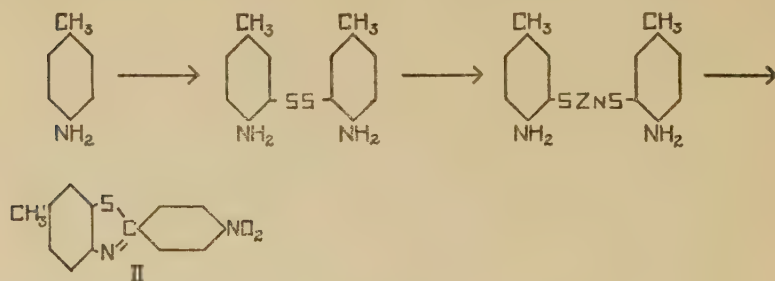


Fusion of this compound with KOH gives p-amino-benzoic acid and 2-amino-5-methyl thiophenol (8). The latter compound was identified in the form of the diazosulfide. Removal of the amino group thru the diazo reaction gave 2-phenyl-6-methyl benzothiazole a compound that had previously been synthesized by Jacobson (1). This latter compound on fusing with KOH gave benzoic acid and the same amino methyl thiophenol as that obtained from dehydro itself (8).

The synthetic proof given by Gattermann and Neuberg (16) is unsatisfactory in one point in that they neglected to isolate and analyze one of the products of the series of reactions. The compound to which we refer is number II below.



Compound number II was never obtained sufficiently pure for either a m.p. or analysis. We prepared II by an entirely different method and obtained an accurate combustion analysis to prove its composition. Our synthetic method is additional proof that formula I above is the correct one for dehydrothio-p-toluidine.

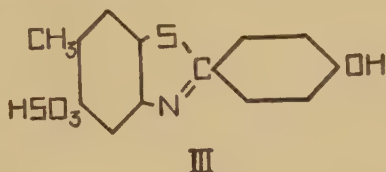


Reduction of (II) with tin and HCl gave (I) above.

The commercial method of preparation of Columbia Yellow depends on alkaline oxidation (usually with NaOCl) of dehydrothio-p-toluidine mono sulfonic acid. Snell has shown that the probable position of the HSO_3 group is position 5 (47). There

are several reactions that might take place on the oxidation of such a compound. The 2-phenyl part of the molecule might be oxidized to a quinone or quinone-imine structure. Further with NaOCl as the oxidizing agent there is the added possibility of chlorimine and chloramine types. Hypochlorites are known in some instances to oxidize methyl groups to stilbene types (29).

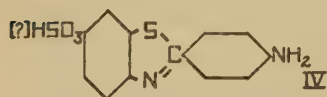
We eliminated the quinone structure as a possibility by preparing the following phenol.



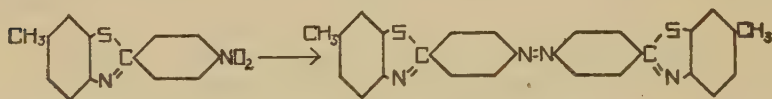
Its constitution was known to be that shown above as it was prepared directly from dehydrothio-p-toluidine sulfonic acid of known structure. The amino group of the latter compound was diazotized and then hydrolyzed with dilute sulfuric acid. A combustion analysis showed the percentage composition to be correct. If the quinone structure for Columbia Yellow were correct a compound of the above type should oxidize as readily as the analogous amino type to form the dye. Alkaline oxidation of the phenol with NaOCl, and with potassium ferricyanide gave no color whatever. Besides eliminating the quinone structure this experimental work made the stilbene structure seem improbable also. The methyl group being in exactly the same position as in (1) should have given a yellow dye with the OH acting simply as an auxochrome if the stilbene structure were correct. As reported above no trace of a dye was obtained.

The possible chlorinated structures mentioned above were eliminated by a quantitative analysis for chlorine. Only a trace of chlorine was found in purified Columbia Yellow. All quinone-imine types are very sensitive to reducing agents and acids. Columbia Yellow is very resistant to both of these reagents.

To further check our conclusions eliminating the stilbene structure we prepared a product analogous to (I) but leaving off the methyl group. We prepared 2(p-amino phenyl) benzothiazole-6-sulfonic acid thru the following series of reactions.



At this stage it appeared likely that the correct structure for Columbia Yellow was an azo structure. We tested out this assumption by reducing 2(p-nitro phenyl) benzothiazole by methods that are usually employed for making azo compounds from nitro compounds, that is, alkaline reduction in alcohol with zinc dust.

Cc1cc(S(=O)(=O)O)ccc1N=C2C=CC=CC2=N=N3C=CC=CC3=C4C=CC(=C4)S(=O)(=O)O

EXPERIMENTAL PART

Purification of commercial Columbia Yellow

Since the commercial product is made by a salting out process it was to be expected that it would contain considerable sodium chloride. A qualitative test for inorganic chlorides on the original dye gave a heavy precipitate of AgCl . The dye being a sulfonic acid interferes with this test if it is carried out in the ordinary way by dissolving in water and adding AgNO_3 . It was first necessary to remove the dye from solution using 50% sulphuric acid. After filtering off the flocculent brown precipitate the test was carried out in the usual way on the clear filtrate.

Two methods of purification were used to obtain a pure sample for analysis. The first involves the isolation of the dye as the free sulphonic acid derivative rather than as the sodium salt, the form in which it comes on the market. The second method makes use of the extreme insolubility of the cerium salt of Columbia Yellow. In neither case was the purified product crystalline. The precipitated dye is decidedly colloidal and very difficult to filter. The fact that the dye is a sulphonic acid and in addition has a high molecular weight, both contribute toward making it colloidal in nature.

Method (1)—Precipitation as the free sulphonic acid

25 g. of the dye were dissolved in 500 cc. of water. Part of the commercial product settled out as an insoluble sediment. Filtered with suction. Using a moderate suction gives better results than strong suction as the latter plugs the pores of the filter more quickly. In any case the filtration is very slow.

To the clear wine red filtrate were added 50 cc. of 50% H_2SO_4 . The free sulphonic acid separated as a reddish brown flocculent precipitate. To facilitate filtering this suspension was allowed to settle out over night and the clear supernatant liquid siphoned off. This liquid tho apparently clear is difficult to draw thru the filter. The dye when collected on the filter had a deep blood red color. This red product was removed from the filter while still moist and pressed out on a porous plate. It dried to a black brittle mass which was powdered and washed with water, first by decantation and then on the filter. Some of the dye is lost by this washing but it is more "slowly" soluble than the inorganic impurities hence a partial separation can be effected. One washing however is not sufficient. The whole of the above procedure was repeated four times to obtain a sample for combustion analysis. We purposely permitted large losses of the dye in the separations as our object was one of purity rather than yield.

Method (2)—Precipitation as insoluble cerium salt

A water solution of the dye was treated with a water solution of cerium nitrate in the ratio of 3 mols of the dye to 2 mols of cerium nitrate. 20 g. of the dye were precipitated from 2000 cc. of solution. Cerium was selected in preference to any other metal as it formed the most insoluble salt of any of the metals that we tried. This method of purification is very advantageous for complete removal of all inorganic impurities. The powdered cerium salt can be washed with large volumes of water with practically no loss of the dye in the washings. Besides removing inorganic impurities this washing removes any organic sulphonic acids of lower molecular weight than Columbia Yellow. It is a fairly general rule that the rare earth salts of the aromatic sulphonic acids increase in solubility with decreasing molecular weight (32). The salt when thoroughly washed and dried is ready for analysis. The cerium may be determined simultaneously with the C and H in a combustion furnace by igniting to cerium dioxide.

PROPERTIES OF COLUMBIA YELLOW NOT REPORTED IN THE LITERATURE

Physical Properties

We have found the dye in the powder form to vary in color from yellowish brown to brick red. The red product has the highest degree of purity. A sprinkling test (35) on a high grade commercial sample showed the dye to be of uniform composition. No differences of shade whatever could be detected in the various particles. It is only very slightly soluble in acetic acid and alcohol but these solvents do not force it out of solution once it is dissolved in water. It is insoluble in all of the common organic solvents.

Chemical Properties

Hydrogen peroxide (3%) has no effect on the dye. Tests were made in both hot and cold, and acid and alkaline solutions. All tests were ineffective in altering the dye.

Oxidation of Columbia Yellow with alkaline potassium permanganate for a period of two months with occasional heating on the steam bath did not destroy the color of the dye nor its ability to dye cotton directly. The dye thus obtained was brighter red in color in the powder form than the original Columbia Yellow. Dyeings made on cotton with this oxidized dye gave a pure yellow color very much like that of Columbia Yellow but somewhat brighter in shade. Because of the length of time which we gave the oxidation it is very probable that the methyl groups were completely oxidized to carboxyl groups. The azo linkage was not destroyed.

Stannous chloride and HCl, when added to a boiling solution of Columbia Yellow caused the solution to be immediately decolorized and a black precipitate formed. This reduction was carried out in the manner described by Green (36) for splitting azo dyes. The black product when dried and ground up had a metallic lustre. In appearance it was much like the free sulfonic acid of Columbia Yellow but differed decidedly from the latter in being entirely insoluble in water. Dilute alkali readily changes it to a soluble red product which when dissolved forms a reddish yellow solution very similar to that of Columbia Yellow. Dyeings were made on cotton and the yellow shades obtained were so nearly like those of Columbia Yellow that we were unable to tell the difference.

The reduction of Columbia Yellow with sodium hydrosulfite was carried out in the following manner. Five g. of the dye, purified as the free sulfonic acid, were dissolved in 500 cc. of boiling water. To this boiling solution was added a solution containing 20 g. of sodium hydrosulfite in 100 cc. of water. The dye solution became brownish black in color. Boiling was continued for 3 hours. Twenty cc. of 50% sulfuric acid were then added and a chocolate brown precipitate settled out. This precipitate did not have the appearance of Columbia Yellow precipitated in a similar manner. The precipitate was filtered and then washed with water. Dissolved in 10% alkali, filtered and again precipitated with 50% sulfuric acid. Filtered and dried on porous plate. The dried product was brownish black in appearance. It dissolves in alkali giving a reddish yellow solution. Two per cent dyeings made with this solution gave a fast yellow shade on cotton which was a trifle lighter than that of Columbia Yellow.

Metallic Salts of Columbia Yellow

In seeking for an insoluble salt to use as a method of purification of the dye from soluble inorganic impurities we prepared the following metallic salts: Ce, Th, Ca, Ba, Cu, and Ag. Roughly the solubility of the salts increases in the order of the salts named, the Ce salt being the most insoluble. We could not detect any appreciable difference in the solubility of the Ce and Th salts. There was a decided difference in solubility between the Ce and Ca salts. All of the salts were prepared from a simple double decomposition in a water solution of the dye and the inorganic salt. The color of the salts ranges from yellow to red. Those first mentioned in the list were the lightest in color. When we attempted to prepare the Sn salt in the above manner the solution was immediately decolorized and a black precipitate formed indicating both reduction and salt formation.

Method for Carrying out a Direct Dyeing with Columbia Yellow

The quantities which we used in practically all of our direct dyeings were the following:

1 g. unbleached cotton.
20 cc. of .1% dye soln. (.02 g. of dye)
25 cc. water.
4 drops of 10% sodium carbonate.
15 cc. 1% sodium chloride soln.
Heated $\frac{1}{2}$ hour on boiling water bath.

Columbia Yellow as a Vat Dye

We have seen no record of Columbia Yellow being used as a vat dye. The shade was brightened somewhat by using the vat dyeing method instead of the direct method. We carried out the vat dyeing as follows. We used 2 parts by weight of hydrosulfite to one part of dye. The orange red dye solution took on a darker red color when the hydrosulfite was added. We used 20% alkali based on the weight of the cloth taken. The bath was kept at 60 degrees for 4 hours.

THE FREE SULFONIC ACID FORM OF COLUMBIA YELLOW



Physical Properties

The commercial product purified according to method (1) above gave a product that was coal black when dry but red when it is wet. Its solubilities are almost identical in every respect with those of the sodium salt form of the dye. It dyes cotton a fast yellow which is a trifle redder than that of the sodium salt. Washing the cloth with a little alkali however makes the colors identical. Only one organic solvent was found in which it would dissolve to any appreciable extent. It dissolves quite readily in phenyl hydrazine to form a reddish violet solution.

Chemical properties

Reaction with HCl and sealed tube. Two g. of the black sulfonic acid were heated in a sealed tube with 8 cc. of HCl (sp. gr. 1.178) for 56 hours at 105 degrees. Most of the product of the reaction settled out as a black granular precipitate. This black product was extracted twice with 100 cc. of hot conc. HCl. Very little went into solution. The insoluble product was then washed thoroughly with water and dried. It was insoluble in cold water but on long standing colors the solution, yellow. Insoluble in conc. alkali but dissolves in dilute alkali to form a yellow red solution much like that of the original dye. The product after washing with alcohol was dried at 110 degrees for 6 hours. It gave the following combustion analysis:

Sample—.2134 g., Water—.0674g. CO_2 —.3902 g.

Calc. for free sulfonic acid of Col. Yellow, H-3.17% and C—52.80%; Found H—3.53% and C—49.87%

Reaction of free sulfonic acid with aniline. The dye was dissolved in water and then made acid with acetic acid (acetic acid

does not force the dye out of solution when once it has been dissolved in water). When a solution of aniline in acetic acid was added a yellow precipitate of the aniline salt separated out immediately. Ortho toluidine gives a similar kind of salt. The salts differ from the sulfonic acid in being insoluble in water and yellow in color.

ANALYTICAL DATA ON FREE SULPHONIC ACID

(Purified commercial product)

Moisture content of air dry sample (air dry 4 days)

Sample—.8982 g. Loss of weight by drying 8 hours at 120° degrees—.0964 g. Found per cent water—10.73%.

Combustion analysis. (Sample dried to constant weight at 120° degrees)

Sample—.2139 g. Water—.0587 g. CO₂—.3916 g.

Calc. for C₂₈H₂₀O₆N₄S₄: H—3.17, C—52.80%

Found: H—3.07, C—49.93%

The Carius method was used for determining sulfur.

Sample—.1968 g. BaSO₄—.2930 g.

Calc. for C₂₈H₂₀O₆N₄S₄: S—.20.11%, Found S—20.40%.

A Carius determination for halogens showed only a trace of Cl present. The low result on C and the high result on S seem to indicate that the dye is slightly over sulfonated.

CERIUM SALT OF COLUMBIA YELLOW

Physical Properties

This salt was prepared as directed in the purification method. (2) above. The air dry product is maroon red in color and very insoluble in water and organic solvents. When freshly precipitated it is reddish yellow and decidedly colloidal in nature. It is very difficult to filter from such a solution.

Moisture content of air dry sample. (air dry 4 days)

Sample—.8397 g. Loss of water by drying to constant weight: at 120 degrees—.1177 g. Found per cent of water—14.02%.

Combustion Analysis.

(Sample was dried at 120 degrees for 8 hours.)

Sample—.2539 g. Water—.0605 g. CO₂—.3987 g.

Calc. for C₈₄H₅₄O₁₈N₁₂S₁₂Ce₂: H—2.49%, C—46.16%

Found: H—2.67%, C—42.83%

Analysis for Cerium by ignition to CeO₂.

Sample—.2213 g. CeO₂—.0349 g. Found % Ce—12.84%

Sample—.2539 g. CeO₂—.0536 g. Found % Ce—13.65%

Calc. for C₈₄H₅₄O₁₈N₁₂S₁₂Ce₂: Ce—12.85%

Chemical Molecular Weight

Averaging the two results obtained above for Ce we obtain the figure for Ce as 13.25%. With only one Ce atom to the mole-

cule a minimum molecular weight would be 1058. The molecular weight of the Ce salt of dehydrothio-p-toluidine-mono sulfonic acid is 1091. It has been our experience and the experience of previous investigators that the salts of dehydro sulfonic acid itself and other benzothiazole sulfonic acids of approximately the same molecular weight have no dyeing power whatever. The azo structure which we believe to be correct from synthetic as well as analytical evidence requires a molecular weight of 2184. Doubling the minimum molecular weight which we found above gives the found molecular weight to be 2116.

SYNTHETIC WORK RELATED TO COLUMIA YELLOW

2(p-benzene diazo chloride) 6-methyl benzothiazole-5-sulphonic acid

This product has been previously reported (6). It is described as a very stable yellow product stable to boiling water. No properties other than this have been given. For the benefit of later workers in this field we will record a few additional properties which may be useful in identifying and working with it.

In preparing this product we used two methods which gave equally good results. The first method was that of Erdmann (3) keeping a constant excess of nitrous acid thruout the reaction in order to eliminate the possibility of coupling. This precaution proved to be unnecessary since when the ordinary method of diazotizing was used no coupling occurred. The latter method is simpler to carry out and since the yield is just as good as in the first it is the more satisfactory one to use. Forty-five g. of the dehydrothio toluidine mono sulfonic acid gave a yield of 45.3 g. of the diazonium salt.

The diazonium salt is very similar in color to the unchanged amino compound from which it is made. It is very slightly soluble in water, amyl alcohol, and acetic acid. It differs from the amino compound in not being readily soluble in cold dilute sodium carbonate. It dissolves in conc. sulfuric acid to form a yellow solution which shows no fluorescence.

2(p-hydroxy phenyl) 6-methyl benzothiazole-5-sulfonic acid

This compound was prepared by hydrolysis of the above diazo salt. The ordinary methods employed to make phenols from diazo compounds did not work in this case. The presence of an HSO_3 group on the nucleus seems to give added stability to the diazo group. The hydrolysis is best carried out by using 20% sulfuric acid. Two g. of the diazo compound were dissolved in one litre of 20% sulfuric acid and boiled for 7 hours. The solution was filtered hot and on cooling the phenol crystallized out as small yellow orange plates. The yield was 1.46 g. (82.52%) of crystalline product. It was recrystallized from a large volume of water.

Water of Crystallization.

The air dry sample was dried to constant weight at 150 degrees..

Sample—.4936 g. Loss of water—.0701 g.

Calc. for $C_{14}H_{11}O_4NS_2 \cdot 3H_2O$ % water—14.40

Found: % water—14.20

Combustion analysis.

Sample—.1866 g. Water—.0583 g. CO_2 —.3327 g.

Calc. for $C_{14}H_{11}O_4NS_2$: H—3.43, C—52.30%

Found: H—3.50, C—52.22%

Properties

A distinctive and striking property is the color it forms with conc. sulfuric acid. It dissolves to form an opalescent solution with a bright sky blue fluorescence. This is in contrast to the analogous NH_2 compound which under the same conditions forms a pale yellow solution with only a very slight blue fluorescence. The phenol is readily soluble in hot alcohol. To purify for analysis it was recrystallized from hot water. It is readily soluble in 10% sodium carbonate forming a clear solution with a very slight blue fluorescence. With ferric chloride in alcohol solution this phenol does not give a color reaction. No change whatever was observed when the ferric chloride was added. The analogous phenol of the same structure but lacking the HSO_3 group gave a similar negative test with ferric chloride.

Methylation of the phenol with dimethyl sulfate using the method of Ullmann (28) gave a yellow product which gave qualitative reactions showing that methylation of the OH group had taken place. The phenol itself readily decolorizes potassium permanganate. The methylated product requires long standing before any decolorization takes place. The methylated product gives a distinctly greener blue fluorescence when dissolved in sulfuric acid than the non-methylated product. We did not obtain a sample sufficiently pure for a combustion analysis.

Bis (2-amino-5-methyl phenyl) disulfide

We prepared this compound according to the directions given by Mandelbaum (48). From 535 g. of para toluidine we obtained 86 g. of the disulfide, a yield of 13.01%. This yield is based on the original amount of para toluidine taking no account of the para toluidine recovered. We used 10% sulfuric acid for extracting the melt in place of benzene as recommended by Mandelbaum. Our yield was about three times that reported by him.

Zinc Salt of 2-amino-5-methyl thiophenol

10 g. of crude bis (2-amino-5-methyl phenyl) disulfide in the form of a yellow brown powder were dissolved in 200 cc. of boiling acetic acid. 20 g. of zinc dust were added during 10 minutes. Refluxed for one hour. Filtered hot and diluted with two volumes of water. The zinc salt separated out as a pure white minutely crystalline product. After washing with water and drying at 110 degrees the product weighed 3.37 g.

2(p-nitro phenyl) 6-methyl benzothiazole

3.22 g. of the above finely pulverized zinc salt were mixed thoroughly in a mortar with 4.2 g. of p-nitro benzoyl chloride. Heated in an open test tube for one hour on a water-calcium chloride bath keeping the temperature at 110 degrees. The mixture first fused to a pasty mass and then during the course of the reaction solidified to a hard cake. The cake was ground up and warmed on a steam bath with 75 cc. of N NaOH to remove any unchanged nitro benzoyl chloride. The remaining insoluble product was crystallized from glacial acetic acid. It crystallizes as pale yellow needles having a m.p. of 230 degrees (corr). One crystallization usually gave a product melting at 217-220. Recrystallizing to constant melting point gives 230 degrees. The yield of the pure product was 1.5 g. It is readily soluble in chloroform, toluene and carbon disulfide; moderately soluble in acetic acid and acetone; slightly soluble in alcohol and insoluble in petroleum ether. Acetic acid is the best crystallizing solvent. It dissolves in conc. sulfuric acid to form a pale yellow solution.

Combustion analysis.

Sample—.1838 g. Water—.0638 g. CO₂—.4188 g.

Calc. for C₁₄H₁₀O₂N₂S: H—3.70%, C—62.22%

Found: H—3.88%, C—62.14%

2(p-azo phenyl) 6-methyl benzothiazole

1.5 g. of 2(p-nitro phenyl) 6-methyl benzothiazole were dissolved in 200 cc. of boiling alcohol. To this boiling solution were added 4.5 g. of NaOH in 27 cc. of water. During the course of one hour 13 g. of zinc dust were added in small portions. At first the solution became orange red in color indicating the formation of the azo compound. After refluxing two hours the solution became grayish yellow indicating that the hydrazo compound had been formed. The hot solution was filtered with suction. The filtrate changed very rapidly to an orange red color. To insure completeness of reoxidation to the azo product air was passed into the solution for six hours. On standing a bright colored orange red product settled out. It was purified by first washing with a small amount of dilute HCl to remove any amino or hydrazo impurities. It was then washed successively with warm glacial acetic acid to remove any unchanged nitro product and finally with alcohol and water. It crystallizes from glacial acetic acid in the form of an orange red microcrystalline powder. The azo product is only slightly soluble in acetic acid hence a large volume of solvent is necessary when the latter is used as a crystallizing solvent.

Combustion analysis.

Sample—.1507 g. Water—.0590 g. CO₂—.3893 g.

Calc. for C₂₈H₂₀N₄S₂: H—4.20%, C—70.59%

Found: H—4.38%, C—70.45%

2(*p*-azo phenyl) 6-methyl benzothiazole does not melt below 250 degrees. Above 250 degrees it gradually decomposes as the temperature is raised. It dissolves in conc. sulfuric acid to form a brilliant carmine red solution. Only a very small amount of product is necessary to give this reaction. (The analogous amino and nitro compounds give only a pale yellow solution in conc. sulfuric acid.) Careful dilution of the sulfuric acid solution causes the sulfuric acid salt to separate out as yellowish red crystalline plates.

Sulfonation of 2(p-azo phenyl) 6-methyl benzothiazole

The sulfonation was carried out under the same conditions as those used for making the monosulfonate of dehydrothio-p-toluidine (6). 1.5 g. of the above azo compound were dissolved in 50 cc. of conc. sulfuric acid. The solution was cooled to 20 degrees. 20 cc. of fuming sulfuric (50% free SO₃) were added slowly never allowing the temperature to rise above 50 degrees. Warmed on a water bath for 5 hours keeping the temperature between 40 and 50 degrees. When poured upon ice a yellow orange precipitate settled out. It was allowed to stand one hour before filtering. While wet the product was reddish brown. On drying it became brownish black very similar in appearance to the free sulfonic acid form of Columbia Yellow. Yield 1.7 g.

This black product proved to be identical in every respect with the free sulfonic acid form of Columbia Yellow. It dissolves very readily in water to form a wine red solution. Comparative dyeings were made on cotton using the purified commercial product and the azo product as prepared above. The dyeing conditions were kept exactly the same in both cases. Both products gave shades which were very strikingly alike. They both responded equally well toward alkali and acid fastness tests. Every comparative test which we made indicated that the two dyes were identical.

O-dinitro phenyl disulfide

We used the method of Wohlfahrt (27) in preparing this substance. There was no difficulty in obtaining a 73% yield of pure product.

Zinc salt of o-amino thiophenol

To prepare this we followed the method given by Snell (46). Our yields in this case were not as high as reported in the dissertation.

2(p-nitro phenyl) benzothiazole

This also was prepared according to the directions given by Snell (46). We did not take the trouble to get the product to a high standard of purity at this stage as the product of the next step in the series was the one that we were most interested in.

2(p-amino phenyl) benzothiazole

We carried out the reduction of the nitro compound in the man-

ner described by Snell (47) with the exception that we used considerably more HCl.

2(p-amino phenyl) benzothiazole-6(?) -sulfonic acid

To prepare this compound we sulfonated 2(p-amino phenyl) benzothiazole in the same manner in which the monosulfonate of dehydrothio-p-toluidine is made (6). 5 g. of 2(p-amino phenyl) benzothiazole were dissolved in 20 cc. of conc. sulfuric acid. Cooled to 25 degrees and then added 15 cc. of fuming sulfuric (50% free SO_3) never allowing the temperature to rise above 50 degrees. Heated for 8 hours at 40-50 degrees. A drop of the sulfonation mixture tested with dilute ammonia showed the sulfonation to be complete. When poured upon ice a flocculent bright yellow precipitate settled out. This yellow product was obtained in crystalline form by dissolving in a warm solution of dilute alkali and adding acetic acid until the first cloudiness appeared. The product crystallized as silky white flakes. The yield of crystalline product was 5.1 g. Analysis for water of crystallization in the air dry product gave the following results. Sample—.8225 g. Loss of water on drying to constant weight at 110 degrees. .0647 g. Found % loss of weight 7.87%. Calc. for $1\frac{1}{2}$ moles of water—8.10%.

Combustion Analysis

Sample—.1535 g. Water—.0479 g. CO_2 —.2849 g.

Calc. for $\text{C}_{13}\text{H}_{10}\text{O}_3\text{N}_2\text{S}_2$: H—3.30%, C—50.95%

Found: H—3.49%, C—50.62%.

A new yellow dye from 2(p-amino phenyl) benzothiazole-6(?) -sulfonic acid

This dye was prepared to show the effect of the absence of a methyl group in dyes of the Columbia Yellow type. In preparing this dye we used the hypochlorite method described in the German patent (12) for making Columbia Yellow from the monosulfonate of dehydrothio-p-toluidine. We obtained a yellow dye of much lighter yellow shade than Columbia Yellow. It dyes cotton directly and is fast to alkali and acids. We were able to conclude from this that the methyl group is responsible for deepening of the shade but is not necessary for yellow color or for cotton fastness.

BIOGRAPHICAL

Frank H. Bergeim was born in Brookings, South Dakota, April 4, 1897. He received the degree of B.S. from South Dakota State College in 1919. During the years 1919-1921 he was chemistry assistant and research fellow at Northwestern University from which institution he received the degree of M. S. in 1921. The work of his Master's dissertation was published with W. Lee Lewis in the Journal of the American Chemical Society **43**, 891. (1921). For the past three years he has been a laboratory and analytical assistant in the department of Organic Chemistry at Columbia University.

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